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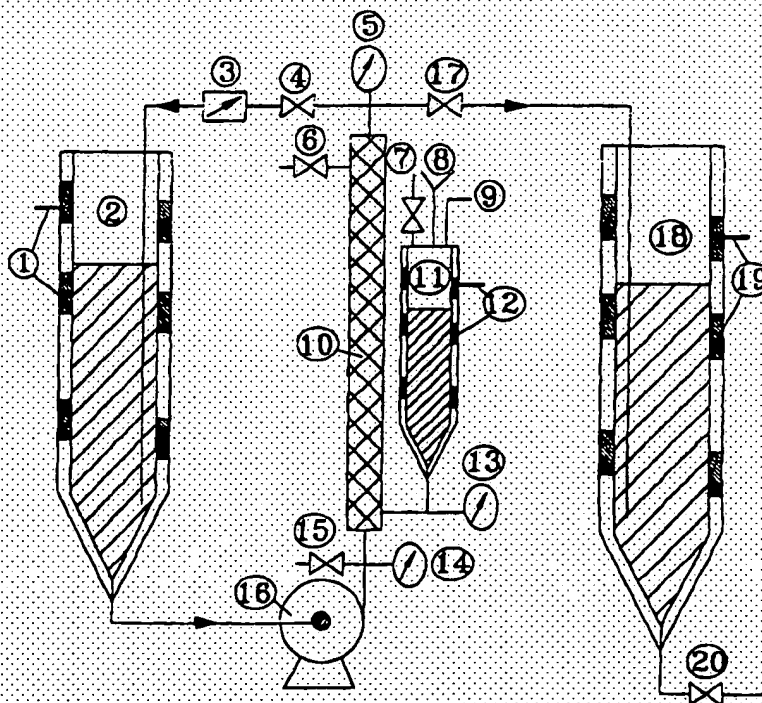
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(54) Title: DISPERSION OF IMMISCIBLE PHASES

## (57) Abstract

A method for preparing a mixture of the emulsion type wherein a discontinuous phase is introduced into a circulating continuous phase by passage through a membrane which preferably consists of a ceramic or sintered metal material.



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### DISPERSION OF IMMISCIBLE PHASES

This invention relates to an apparatus and method for producing dispersions of two or more immiscible phases, for example in the manufacture of emulsions and encapsulated products wherein the properties of the dispersed phase droplets must be carefully controlled.

The production of oil-in-water and water-in-oil emulsions and other multiphase mixtures is of significant economic importance worldwide but the method of manufacture can be problematical, especially in scale-up from laboratory to pilot and production levels. For example, emulsions are often made in batches and variations between batches occur since the process may be irreproducible during large-scale manufacture.

For example, most existing methods of emulsion manufacture rely on the establishment of turbulent flow in a fluid-mixing regime consisting of two immiscible liquids contained within a single manufacturing vessel. Due to turbulent eddies produced by vigorous stirring, one phase is broken up into droplets (the discontinuous phase) which becomes suspended in the other (continuous) phase. The size and size-distribution of these droplets is of critical importance, since it determines the stability of the emulsion against coalescence and its suitability for intended use. For a given pair of phases processed by this existing method, the droplet size is determined primarily by the size of the turbulent eddies and the time exposure to those eddies. There have been proposed in the literature (Walstra, Encyclopaedia of Emulsion Technology, Vol. 1, 1983, Belcher (Ed), Dekker, New York)) relationships which correlate the droplet size with the energy input (through agitation) per unit volume. The value of the energy input depends upon the surface tensions of the liquids, their density and the power input for an agitator of given geometry. The energy input might typically vary from  $10^4$  watts per cubic meter (for a paddle stirrer) to  $10^{12}$  watts per cubic meter (for a high-pressure homogeniser).

The long-standing problem is that such processes are inefficient because neither can the turbulence be controlled or generated consistently throughout the volume of liquid in large manufacturing vessels, nor can the behaviour of

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any pair of immiscible phases be predicted on a large scale based on experiments in a laboratory. The consequence is that energy is used inefficiently and, more importantly, it is not possible to control the droplet size or the size distribution with any confidence.

Alternative methods have been proposed based, for example, on droplet formation using electrostatic or ultrasonic nozzles; nevertheless the resulting product quality, cost and scalability of these methods are unattractive.

Various methods have recently been proposed wherein a membrane is used to facilitate the mixing of two phases. In Japanese Patent Application No. 2-214537 (published 27th August 1990) there is proposed a method of preparing emulsions wherein the aqueous phase is passed under pressure through the pores of a membrane into an oil phase containing a surfactant, the membrane being subjected to ultrasonic radiation during the process. Nakashima et al., Key Engineering Materials, 1991, Vol. 61-62, pp 513-516, describe a method of preparing emulsions wherein the oil phase is passed through a membrane into an aqueous phase containing a surfactant, a condition being that the oil phase must not wet the membrane. Further work by Nakashima et al. is described in various patent specifications, namely EP 546,174 A1, US 4,657,875 and US 5,326,484. In these, the membrane is made of glass and its pores are of uniform size.

In more specialised technology, EP Specification No. 452,140 A1 describes a method for the manufacture of emulsions by passing one phase into another through a membrane, particularly in the field of making foodstuff spreads. WO Specification No. 87/04924 is addressed to the manufacture of liposomes and involves the use of a commercially-available asymmetric ceramic filter.

According to the present invention there is provided a method for preparing a mixture of the emulsion type wherein a discontinuous phase is introduced into a circulating continuous phase by passage through a membrane which is characterised by at least one of the following features:-

- (a) it consists of a ceramic or sintered metal material;
- (b) it is formed in a plurality of segments which may be identical or different from each other;



- (c) at least one segment is tubular in shape and divergent in diameter along the length of the tube.

According to a further feature of the invention there is provided an apparatus so designed as to enable the method of the invention to be carried out, said apparatus comprising a membrane as defined above together with means for providing a circulating continuous phase, means for providing a discontinuous phase and a source of pressure to force the discontinuous phase through the membrane.

The factors which determine the size of the droplets in the discontinuous phase, and the size-distribution of said droplets, are:-

- (i) the shape, surface chemistry and pore size and size distribution of the membrane;
- (ii) the rate of flow of the continuous phase across the membrane;
- (iii) the pressure under which the discontinuous phase is forced through the membrane;
- (iv) the individual temperatures of the two phases; and
- (v) the interfacial tensions, densities and viscosities of the phases.

The membrane itself is preferably formed from a ceramic material, and more particularly it is preferably substantially tubular in shape with the pores passing radially through the material of the tube. The size and size-distribution of the pores of the membrane will be determined by the type of emulsion desired. For example, if oil phase droplets of diameter 1  $\mu\text{m}$  are desired, a pore size of the order of 0.35  $\mu\text{m}$  will be required. The surface chemistry of the membrane may be adapted to provide varying degrees of wettability.

When the membrane is formed of sintered metal it will preferably have a rolled surface finish.

The method and apparatus of the invention may be adapted to produce either a single-phase emulsion or an emulsion containing a plurality of discontinuous phases, and it may work in either a batch-process or a continuous production mode.

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When a batch-process is desired, the membrane may be formed in the shape of a diverging tube. The continuous aqueous phase is circulated and recirculated through the inside of the tube and the discontinuous oil phase is forced through the tubular membrane wall into the continuous phase. The tube is made divergent in order to maintain constant shear force along the length of the membrane surface, as the total volume and viscosity of the emulsion increase as more oil phase is added to the aqueous phase during passage along the tube. This divergence is however not absolutely essential to the operation of the invention. The pore structure of the membrane may be varied, both in terms of individual pore area and number of pores per unit area of the membrane, to ensure that there is uniformity of droplet size along the length of the tube. The circulation of aqueous phase is stopped when the volume of oil phase in the emulsion has reached the desired level.

When a continuous process is desired, the continuous phase is recirculated via a storage vessel from which the desired emulsion is bled off when the volume of oil phase has reached the desired level.

The membrane may consist of a single tubular structure as described above, or it may consist of a plurality of such tubular structures arranged serially, to form a segmented tubular structure. The individual segments of the tubular membrane may be adapted to permit a plurality of different droplet sizes or size distributions of the same oil phase, or to provide a plurality of different oil phases, with droplet sizes or size distributions which may be the same or different. The surface chemistry and geometry of the membrane itself, and the pressure under which the oil phase is forced through the membrane, can be varied as desired for each of the individual segments.

It is also important that the temperatures of the different oil phases, and indeed that of the continuous phase, may be individually adjusted to optimise the operation of the invention.

According to a further feature of the invention there is provided a method of preparing a mixture of the emulsion type wherein the discontinuous phase consists of an encapsulated substance, which comprises the use of a segmented membrane of the type described above wherein a first segment distributes a discontinuous phase into a continuous phase, and a further segment distributes a further discontinuous phase which coats the first discontinuous phase.

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The initial emulsion is prepared as generally described above. The encapsulation process may then be carried out, for example, by passing the initial emulsion through a conical tube into a narrower-bore membrane tube incorporating a flow-splitter along its axis to reduce the effective flow area between the splitter and the membrane surface. The further oil phase introduced into the narrower-bore membrane tube, by means generally described above, then forms a coating on the droplets of the initial oil phase. It must be understood that the surface properties of the further membrane are important in controlling the oleophilicity of the further oil phase and thus improving the coating of the initial oil phase.

According to a further feature of the invention there is provided a method of controlling the start-up of an emulsification process as described above, which comprises the use of on-line measurements of the size and size-distribution of the initially-formed discontinuous phase droplets as a feed-back signal to control the cross-flow velocity of the continuous phase and thereby ensure that the desired size and size-distribution of the final discontinuous phase droplets are obtained.

The on-line measurements may be obtained by the use of laser scanning microscopy, conductivity measurements and/or other suitable measurement methods. These measurements may separately be used to provide quality assurance of the desired product.

The invention is further illustrated but not limited by way of example with reference to the following drawings:-

In the first embodiment, exemplified in Figures 1 to 8,

Figure 1 shows a schematic diagram of a single module cross-flow membrane unit which comprises:-

- (a) a vessel (2) containing the aqueous phase which is adapted to provide for the recirculation of that phase;
- (b) a vessel (11) containing the oil phase;
- (c) a membrane cross-flow unit (10) through which the oil phase may be passed into the aqueous phase; and
- (d) a final product vessel (18).

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Both vessels (2) and (11) are provided with heating means (1) and (12) respectively and vessel (18) is provided with cooling means (19). Vessel (11) is further provided with filling means (8) and a source of pressure (9). The various pumps, gauges and valves which interconnect the vessels will hereinafter be described under the description of the procedure for operation.

The membrane unit (10) is shown in more detail in Figure 1(a). The cylindrical membrane itself (25) is supported by a (usually stainless steel) body (22) and a further (usually stainless steel) concentric body (26), separated from (22) by seals (23) and adjustable by clamp means (29), provides a chamber (24) for the oil phase. Entry means are also provided for a gaseous purge (21), for the oil phase (27) and for the aqueous phase (28).

In operation, vessel (2) is filled to the appropriate level with the aqueous phase through valve (4), valve (17) and sampling valve (15) being closed. Vessel (11) is filled to the appropriate level with the oil phase, suitably emulsified, through funnel and valve (8), purging and pressure valve (9) being open and valve (13) closed. The contents of both vessels are heated to the appropriate temperature by means of the heating tapes (1) and (12). The aqueous phase is then caused to flow through the apparatus by operation of pump (16) and regulation by valve (4) as shown by flowmeter (3) and pressure gauges (5) and (14).

The oil phase in vessel (11) is brought to the appropriate pressure by means of pressure valve (9), initially air being purged from the chamber (24) by having valves (6) and (13) open, valve (8) closed and relief valve (7) set to safety level. When all air is purged, valves (6) and (13) are closed and the oil pressure is brought to and maintained at the appropriate level by means of valve (9). The emulsification process is begun by opening valve (13), the oil phase being forced under pressure through entry (27) and through the membrane (25) into the aqueous phase running through the membrane unit (10).

The process is continued until the volume of oil in the emulsion reaches the desired level. This can be determined by noting the volume of oil phase remaining in vessel (11) and by samples of the emulsion removed through sampling valve (15). Small variation in the rate of flow of the aqueous phase



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can be controlled by valve (4). The process is terminated by closing valve (13) and switching off pressure valve (9). The finished product is transferred to vessel (18) by closing valve (4) and opening valve (17), and may then be cooled to the appropriate temperature by use of jacket (19) and removed from the system through valve (20).

Figure 2 shows a sequence of photographs, taken with a high-speed video-camera, of the detachment of an oil droplet from a pore of a membrane. The data shown are for a coarse pore of 98  $\mu\text{m}$  diameter and a pressure drop of 2 psi. The double-hatched picture represents the final detachment of the droplet from the pore; it can be seen that increasing the cross-flow velocity of the aqueous phase from 0.19 m/s to 0.40 m/s decreases the droplet formation time from 2380 milliseconds to 420 milliseconds.

Figure 3 shows an electron-micrograph of a ceramic membrane surface with a wide range of pore sizes.

Figure 4 shows in graphical form the relationship between pore size distribution, cross-flow velocity of the aqueous phase and predicted oil droplet size distribution. The droplet size distribution can be controlled by varying the pore size distribution as well as by varying the cross-flow velocity.

Figure 5 shows in graphical form the effect of increasing the cross-flow velocity of the aqueous phase on:-

- (a) droplet size;
- (b) number of oil droplets produced per pore per unit time;
- (c) escape velocity of oil droplets from the pore (measured using a high-speed video-camera); and
- (d) Reynolds Number based on the tube diameter of the membrane module.

All data were obtained using a coarse pore size of 98  $\mu\text{m}$  diameter and a pressure drop of 2 psi. It can be seen that increasing cross-flow velocity reduces the size of the oil droplets but increases the production rate thereof.

Figure 6 shows in isometric diagrammatical form the relationship between oil droplet size and:-

- (a) cross-flow velocity of the aqueous phase; and
- (b) pressure drop across the membrane.

Figure 7 shows in graphical form an example of the evolution of droplets per area ( $m^2$ ) of membrane. This example is from a batch production process using a coarse membrane with narrow pore size distribution.

Figure 8 shows a schematic diagram of a segmented membrane tube (corresponding to item 10 in Figure 1) which allows for either two sizes of droplets of the same oil phase (in which case the same type of oil phase will be contained in chambers 1 and 2 and the membranes 3 and 4 will differ from each other) or for two different oil phases (in which case two different oil phases will be contained in chambers 1 and 2 and the membranes 3 and 4 may be the same or different). This system may be extended by the use of additional membrane segments to cater for more than two different oil phases and/or oil droplet sizes.

In a second embodiment, exemplified in Figures 11 to 16,

Figure 11 shows a schematic diagram of a single module cross-flow membrane unit, similar to that shown in Figure 1, which is adapted to provide continuous emulsion production at room temperature. It comprises a continuous (aqueous) phase tank equipped with a stirrer, a discontinuous (oil) phase tank, a washing tank, a continuous phase circulation pump, a pressure gauge and a membrane module, all labelled, and valves numbered 1 to 6 the functions of which are described below.

Figure 11(a) shows the membrane module in diagrammatic form; it is similar to that described in Figure 1(a) and is appropriately labelled. The ceramic element is 600 mm. in length and has a 5 mm. internal diameter. The inner surface may be coated so as to produce a mean pore size in the range of 0.1 upwards, and typically 0.2  $\mu m$ .

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In operation, the two phase tanks are filled with appropriate fluids, the membrane is saturated with aqueous phase and with all valves closed the pump and stirrer (the latter slowly enough to prevent vortex motion) are switched on. By adjustment of the pump the flow rate of the aqueous phase through the membrane is reduced to that desired. Valves 3 and 6 are then opened and air allowed into the system to produce the desired pressure of the oil phase. The emulsification process is then started by opening valve 2.

The droplet-size distribution in the aqueous phase tank was monitored until the desired emulsion had been formed, at which time the process was stopped by closing all valves, releasing the air pressure and stopping the pump and stirrer. The finished product was released from the aqueous phase tank and the system washed out before the next operation.

In a third embodiment, exemplified in Figures 21 to 27,

Figure 21 shows a schematic diagram of a single module cross-flow membrane unit which comprises:-

- (a) a vessel (2) containing the aqueous phase which is adapted to provide for the recirculation of that phase;
- (b) a vessel (43) containing the oil phase;
- (c) a membrane cross-flow unit (14) through which the oil phase may be passed into the aqueous phase; and
- (d) a final product vessel (31).

Both vessels (2) and (43) are provided with heating means (4) and (32) respectively and vessel (31) is provided with cooling means (25). Vessel (43) has a removable lid and is further provided with a source of pressure (39). The various pumps, gauges and valves which interconnect the vessels will hereinafter be described under the description of the procedure for operation.

The membrane unit (14) is shown in more detail in Figure 21(a). The cylindrical membrane itself (46) is supported by a (usually stainless steel) body (52) and a further (usually stainless steel) concentric body (45), separated from (52) by seals (49) and adjustable by clamps (44,48), provides a chamber (50) for the oil phase. Entry means are also provided for a gaseous purge (51), for the oil phase (47) and for the aqueous phase (53).

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In operation, vessel (2) is filled to the appropriate level with the aqueous phase through valve (20). Vessel (43) is filled to the appropriate level with the oil phase, suitably emulsified, through a removable lid. The contents of both vessels are heated to the appropriate temperature by means of the heating tapes (4) and (32). The aqueous phase is then caused to flow through the apparatus by operation of pump (19) and regulation by valve (7), as shown by flowmeter (3) and pressure gauges (12) and (17).

The oil phase in vessel (43) is brought to the appropriate pressure by means of pressure valve (39) and air regulator (38), initially air being purged from the chamber (50) by having valves (47) and (51) open and relief valve (35) set to safety level. When all air is purged, valves (47) and (51) are closed and the oil pressure is brought to and maintained at the appropriate level by means of valve (39) and regulator (38). The emulsification process is begun by opening valves (40, 41), the oil phase being forced under pressure through entry (47) and through the membrane (46) into the aqueous phase running through the membrane unit (14).

The process is continued until the volume of oil in the emulsion reaches the desired level. This can be determined by noting the volume of oil phase remaining in vessel (43) and by samples of the emulsion removed through sampling valve (13). Small variation in the rate of flow of the aqueous phase can be controlled by valve (7) or lobe pump (19). The process is terminated by closing valves (40, 41) and switching off pressure valve (39), thus releasing the pressure drop. The finished product is transferred to vessel (31) by switching valve (22), and may be cooled to the appropriate temperature by use of jacket (25) and removed from the system through valve (30).

Figure 22 shows an accurate representation of the droplets growing at a pore, derived from observations made with a high-speed camera, at given times. The results shown are for a single coarse pore of 98 microns diameter and a pressure drop of 2 psi. It can be seen that increasing the cross-flow velocity of the aqueous phase from 0.19 m/s to 0.40 m/s decreases the droplet formation time from 2380 milliseconds to 420 milliseconds.



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Figure 23 shows:-

- (a) an electron micrograph of a ceramic membrane surface;
- (b) image analysis which reveals the apparent surface pores; and
- (c) a cross-section through the membrane showing an example of the finer coating layer overlying a coarser substrate.

Figure 24 shows in graphical form the effect of increasing the cross-flow velocity of the aqueous phase on:-

- (a) droplet size;
- (b) number of oil droplets produced per pore per unit time;
- (c) escape velocity of oil droplets from the pore (measured using a high-speed video-camera); and
- (d) Reynolds Number based on the tube diameter of the membrane module.

All data were obtained using a coarse pore size of 98  $\mu\text{m}$  diameter and a pressure drop of 2 psi. It can be seen that increasing cross-flow velocity reduces the size of the oil droplets but increases the number thereof.

Figure 6 shows in isometric diagrammatical form the relationship between oil droplet size, cross-flow velocity of the aqueous phase and pressure drop across the membrane.

Figure 26 shows a schematic diagram of a segmented membrane tube (corresponding to item 14 in Figure 1) which allows for either two sizes of droplets of the same oil phase (in which case the same type of oil phase will be contained in chambers 1 and 2 and the membranes 3 and 4 will differ from each other) or for two different oil phases (in which case two different oil phases will be contained in chambers 1 and 2 and the membranes 3 and 4 may be the same or different). This system may be extended by the use of additional membrane segments to cater for more than two different oil phases and/or oil droplet sizes.

Figure 27 shows the droplet size distribution manufactured using a dual membrane assembly (as described in Figure 26) having mean pore diameters of 0.5 microns and 4.0 microns, and operated at 40 psi and 10 psi respectively.

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In the Examples set out below, all % compositions are weight/weight.

#### Example 1

An aqueous phase was prepared by adding sorbitol mono-oleate ("Span" 80) (2.5%) to a stirred solution of polyoxyethylenesorbitan mono-oleate ("Tween" 20) (2.5%) and (sodium "Nipastat") (0.3%) in water (64.7%) and the mixture was loaded into the aqueous phase tank of an apparatus as described in Figure 11. Mineral oil (30.0%) was loaded into the oil phase tank and the emulsification process was carried out for 4.5 hours with an initial crossflow velocity of 5.09 m/sec., to produce a 30% oil-in-water emulsion. The pore size distribution and droplet size distribution are shown in Figure 12; the mean droplet size was 2.03  $\mu\text{m}$ . and the mean pore size was 0.41  $\mu\text{m}$ ., giving a ratio of 4.95. In general terms the droplet size distribution may be described in terms of a distribution coefficient  $\epsilon$  which is defined by the equation:-

$$\epsilon = (D^{90} - D^{10})/D^{50}$$

wherein  $D^{90}$ ,  $D^{50}$  and  $D^{10}$  are the particle sizes obtained when the cumulative frequencies of the emulsion product when measured on a Malvern Instruments Mastersizer are 90%, 50% and 10% respectively. For a perfect monodisperse system  $\epsilon$  is zero. In the present Example the emulsions produced give an  $\epsilon$  value of not more than 0.6, and at best not more than 0.3. The distribution of pore sizes in the membrane can be defined by the same  $\epsilon$  being not more than 0.6 and that no single pore has a size greater the 150% of the mean pore size. The droplet size and size distribution remained unchanged for several weeks, although there was some early phase separation. Figure 12(a) shows a photomicrograph of the product (magnification x 400); the striations in the image are caused by marks on the camera lens.

#### Example 2

An aqueous phase consisting of a solution of triethanolamine (3.0%) and sodium "Nipastat" (0.3%) in water (66.7%) was loaded into the aqueous phase tank of an apparatus as described in Figure 11. A solution of isostearic acid (3.0%) in mineral oil (27.0%) was loaded into the oil phase tank and the

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emulsification process was carried out for 6 hours with four different crossflow velocities. Figure 13(a) shows the pore size distribution (identical with that shown in Figure 12) and Figure 13(b) shows the droplet size distribution for each of the four velocities. The crossflow velocities are given as a range, because as the concentration of oil in the emulsion increases, it becomes more viscous (as indicated by the reduction in Reynolds number, which is a function of velocity times density divided by viscosity). In practice, the velocity falls by about 10% by the end of the process. The blip on the graph of droplet size distribution at the highest crossflow velocity arises from the inability of the measuring equipment to deal with very small droplet sizes.

Figure 14 shows the relationship between initial crossflow velocity and mean droplet size. There is an almost linear decrease of mean droplet size with increasing velocity.

Figure 15 shows the relationships between the time progression of the process and:-

- (a) concentration of oil in the emulsion (30% by the end of the process);
- (b) mean droplet size;
- (c) crossflow velocity through the membrane; and
- (d) viscosity of the emulsion.

The oil concentration (a) and the viscosity (d) both as expected increase with time and the crossflow velocity (c) falls as explained above. The mean droplet size (b) in practice decreases slightly with time.

Figure 16 shows a photomicrograph of the product of Example 2 when the highest exemplified crossflow velocity (5.09 m/sec) is used; the droplets are smaller than those obtained from Example 1 as shown in Figure 12(a).

Example 3

This example describes by way of illustration the manufacture of a cosmetic-type emulsion at room temperature, and the effect of the cross-flow velocity on the droplets so produced.

An aqueous phase consisting of a solution of triethanolamine (3.0%) and sodium 'Nipastat' (0.3%; a preservative) in water (66.7%) was loaded into the aqueous phase tank (Figure 21, item 2) and a solution of isostearic acid (3.0%) in mineral oil (27.0%) was loaded into the oil phase tank (Figure 21, item 43). Four emulsification processes were then carried out at four different cross-flow velocities in different batch experiments. The results are shown in Figure 28. Curve (1) shows the pore size distribution. Curves (2), (3), (4) and (5) show the droplet size distributions of the product, measured by means of a Malvern Mastersizer, for each of the cross-flow velocities 1.12, 2.49, 4.34 and 5.09 m/s respectively. Figure 29 shows a typical photomicrograph of a product manufactured by this process.

Example 4

This example demonstrates how control of droplet size can be achieved by choice of membrane properties, in particular by choice of pore size.

An aqueous phase was prepared by adding 'Dobanol' (2.96%) and formalin (0.04%) to a well-stirred solution of sorbitol (36%) in water (36%) and was loaded into the aqueous phase tank (Figure 21, item 2). Mineral oil (25%) was loaded into the oil phase tank (Figure 21, item 43) and two emulsification processes were carried out, one using a ceramic membrane tube (Figure 21[a], item 46) of nominal pore size 0.2 micron and the other using a membrane tube of nominal pore size 0.5 micron. The results are shown in Figure 30 in which curves P1 and P2 show the pore size distribution, and curves D1 and D2 show the droplet size distribution measured using a Malvern Mastersizer, respectively.



### Example 5

The process described in Example 4 was repeated (using a ceramic membrane tube of nominal pore size 0.5 micron) except that when the desired oil concentration was reached (after 100 minutes) more aqueous phase was continuously added, and emulsion product was continuously removed, the flow rates being matched to the oil flux rate so that the emulsion concentration in the aqueous phase tank was maintained at that of the final product. Measurements of emulsion concentration, production rate and particle size as a function of time were made using a scanning laser microscope (Type FRBM, Lasentec Corp.). The results are shown in Figure 31; emulsion concentration in Figure 31(a), oil flux rate in Figure 31(b), droplet size number count in Figure 31(c) and droplet size in Figure 31(d). Figure 32 shows the pore size distribution of the membrane (curve 1) and the droplet size distribution (curve 2). It is clear from these results that the use of on-line instrumentation with associated computer control enables continuous production of an emulsion to be achieved.

### Example 6

This example demonstrates the production of a cosmetic emulsion at high temperature and low shear.

An aqueous phase was prepared by slowly adding 'Carbomer' 934 (0.1%) to well stirred water (88.25%) maintained at 80°C. and then slowly adding triethanolamine (1.0%). The solution was loaded into the aqueous phase tank and maintained at 80°C. by use of the heating tape (Figure 21, item 4). An oil phase was prepared by heating a mixture of petroleum jelly (6.5%), mineral oil (2.0%), stearic acid (1.5%), glyceryl monostearate (0.4%) and isopropyl isostearate (0.25%) to 80°C. and was loaded into the oil phase tank and maintained at 80°C. by use of the heating tape (Figure 21, item 32). The emulsification process was carried out at a cross-flow velocity of 0.5 m/s.

Figure 33(a) shows a cryogenic micrograph of the product obtained by the above process, whereas Figure 33(b) shows a similar micrograph of an emulsion prepared by a conventional high shear process. It can be seen that the lamellae stearate phase appears to be ruptured in the conventional high shear process but is largely intact in the present example, the dispersed oil droplets being otherwise identical. The product of the present process has distinctive application properties from the perspective of the user.

#### Example 7

An aqueous phase in the form of a gel was prepared by adding sodium chloride (2.0%) to a solution of sodium lauryl ether sulphate (40%), cocoamidopropyl betaine (10%), cocadiethanolamide (2.0%) and preservative (0.2%) in water (35.8%) and was loaded into the aqueous phase tank. Silicone oil was loaded into the oil phase tank and the emulsification process was carried out using a stainless steel membrane (Figure 21, item 46; mean pore size 40 microns) until the concentration of silicone oil in the product was 10%. The droplet size distribution of the product, which may be used as a shower gel, is shown in Figure 34. It can be seen that the droplet size is comparable with the size of the membrane pore.

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What is claimed is:-

1. A method for preparing a mixture of the emulsion type wherein a discontinuous phase is introduced into a circulating continuous phase by passage through a membrane which is characterised by at least one of the following features:-
  - (a) it consists of a ceramic or sintered metal material;
  - (b) it is formed in a plurality of segments which may be identical or different from each other;
  - (c) at least one segment is tubular in shape and divergent in diameter along the length of the tube.
2. A method as claimed in Claim 1 wherein the membrane consists of a ceramic material and is substantially tubular in shape with the pores passing radially through the material of the tube.
3. An apparatus so designed as to enable the method according to Claim 1 to be carried out, said apparatus comprising a membrane as defined in Claim 1 together with means for providing a circulating continuous phase, means for providing a discontinuous phase and a source of pressure to force the discontinuous phase through the membrane.
4. An apparatus as claimed in Claim 3 wherein the membrane consists of a ceramic material and is substantially tubular in shape with the pores passing radially through the material of the tube.
5. A method of preparing a mixture of the emulsion type wherein the discontinuous phase consists of an encapsulated substance, which comprises the use of a segmented membrane of the type described in Claim 1 wherein a first segment distributes a discontinuous phase into a continuous phase, and a further segment distributes a further discontinuous phase which coats the first discontinuous phase.
6. A method as claimed in any of Claims 1 to 5 wherein the temperatures of the individual phases are able to be individually adjusted.

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7. A method as claimed in claim 1 wherein the membrane consists of stainless steel and wherein the emulsion produced is in the form of a gel.

8. A method of controlling the start-up of an emulsification process as claimed in Claim 1 which comprises the use of on-line measurements of the size and size-distribution of the initially-formed discontinuous phase droplets as a feed-back signal to control the cross-flow velocity of the continuous phase and thereby ensure that the desired size and size-distribution of the final discontinuous phase droplets are obtained.

9. A method as claimed in Claim 8 wherein the on-line measurements are made by use of a scanning laser microscope.



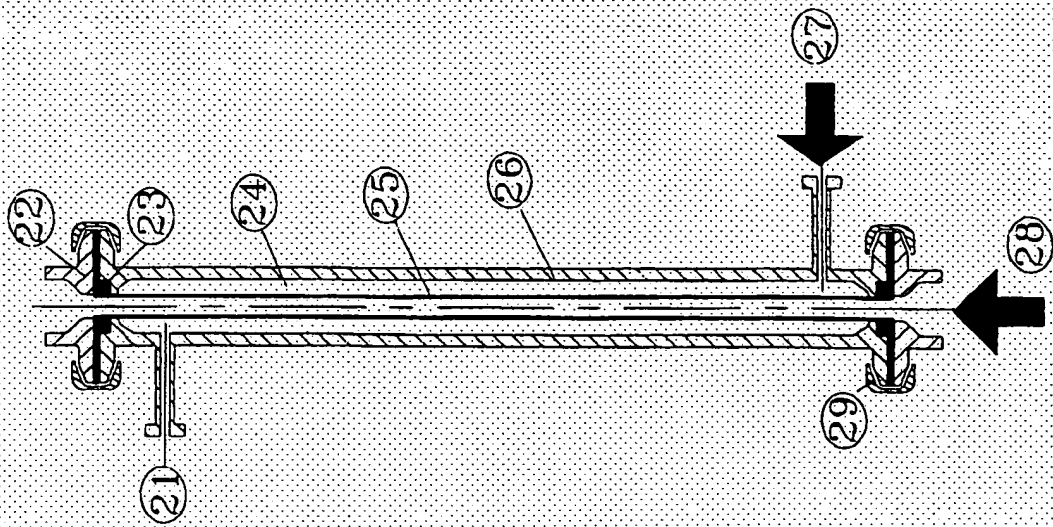


Fig. 1a

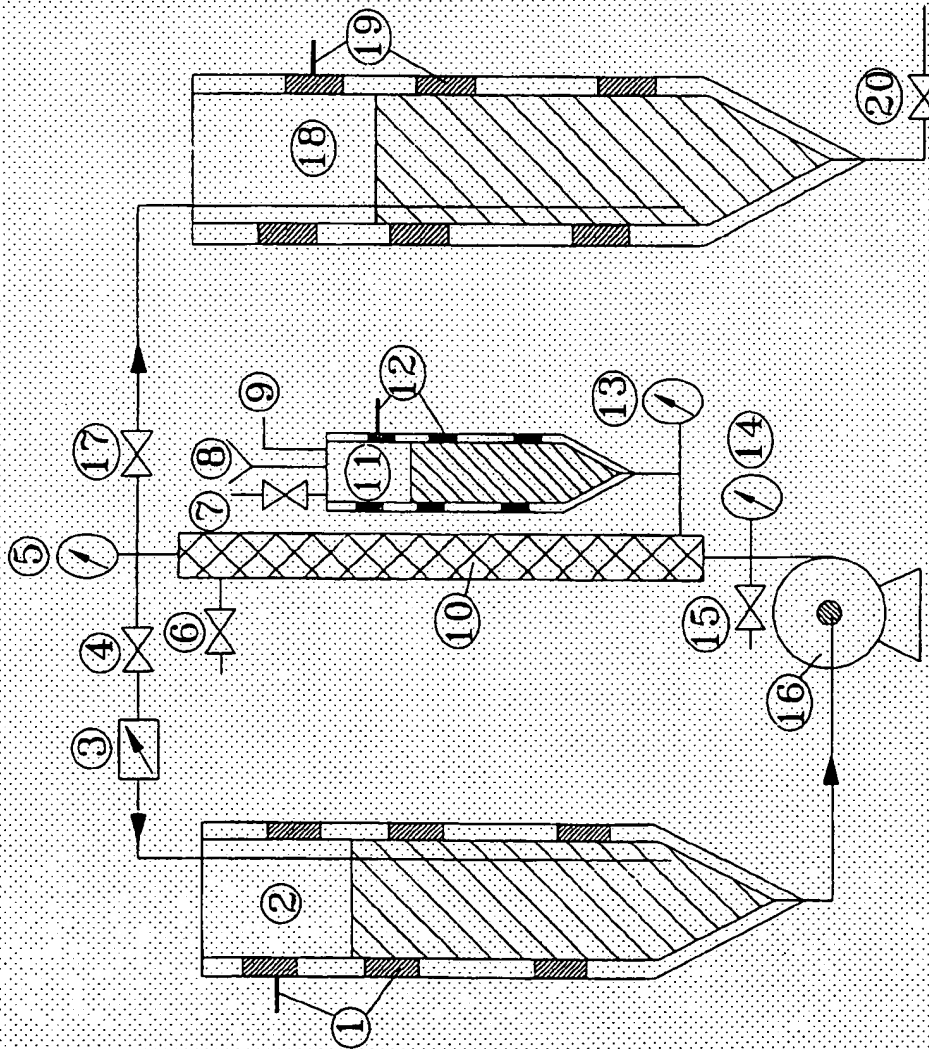








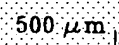


Fig. 1

Time (ms)	0	100	240	420	820	2380
$v=0.19 \text{ m/s}$						
$v=0.40 \text{ m/s}$						



500  $\mu\text{m}$

Fig. 2

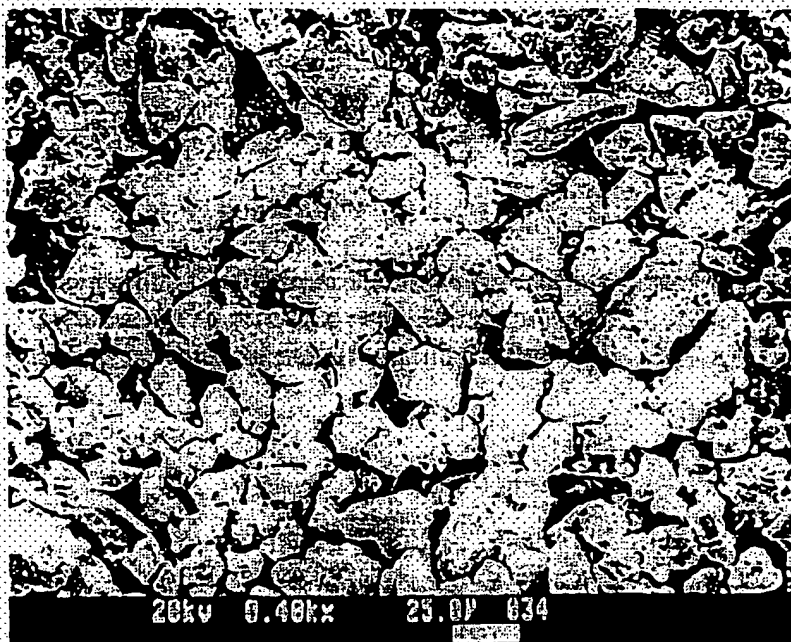


Fig. 3

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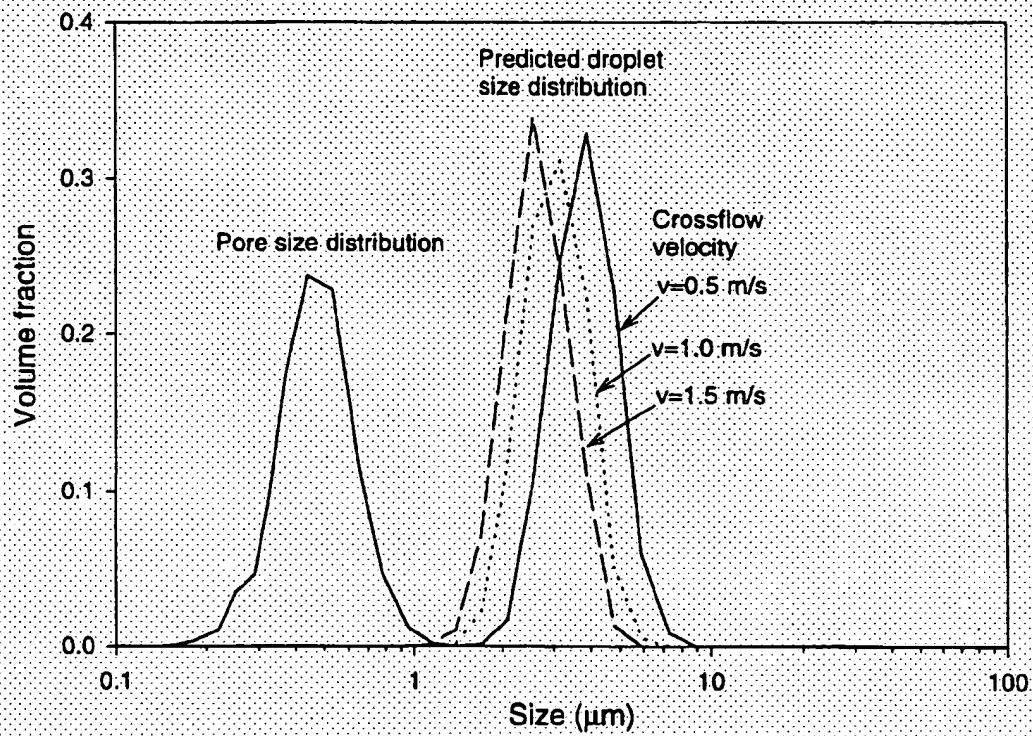


Fig. 4

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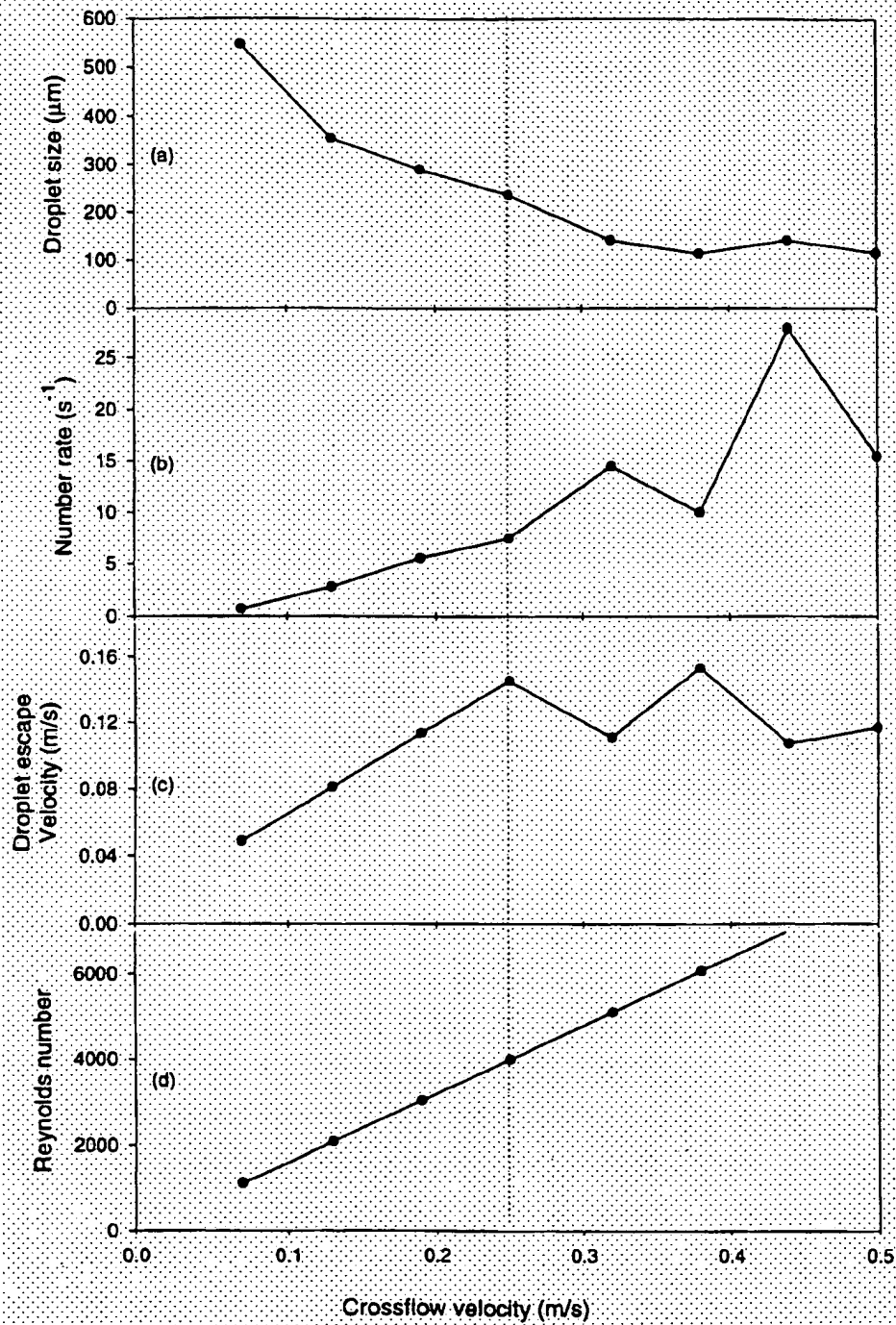


Fig. 5  
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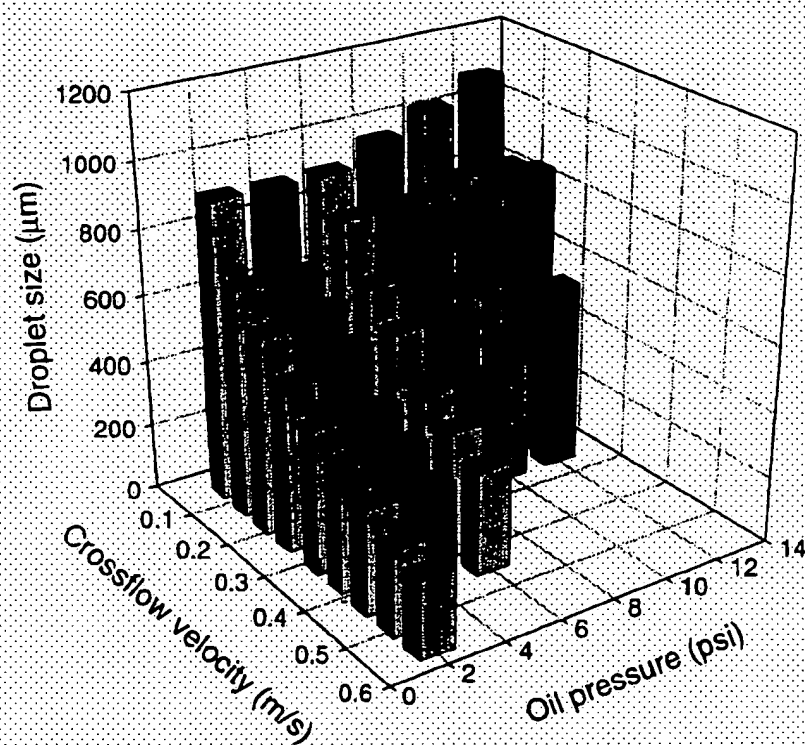


Fig. 6

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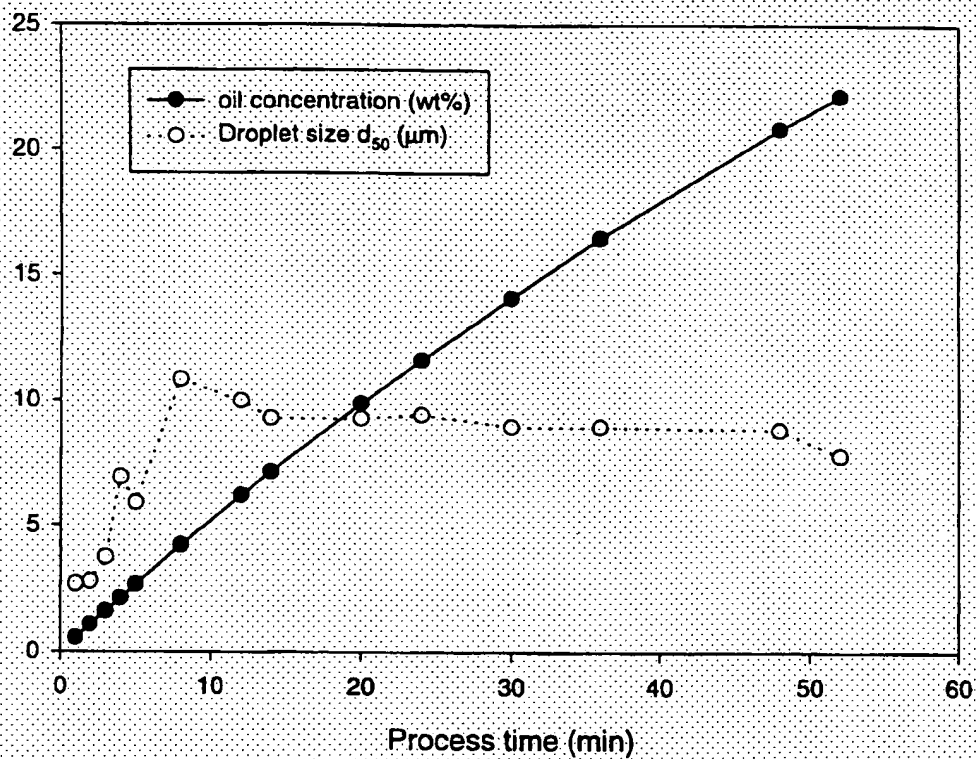


Fig. 7

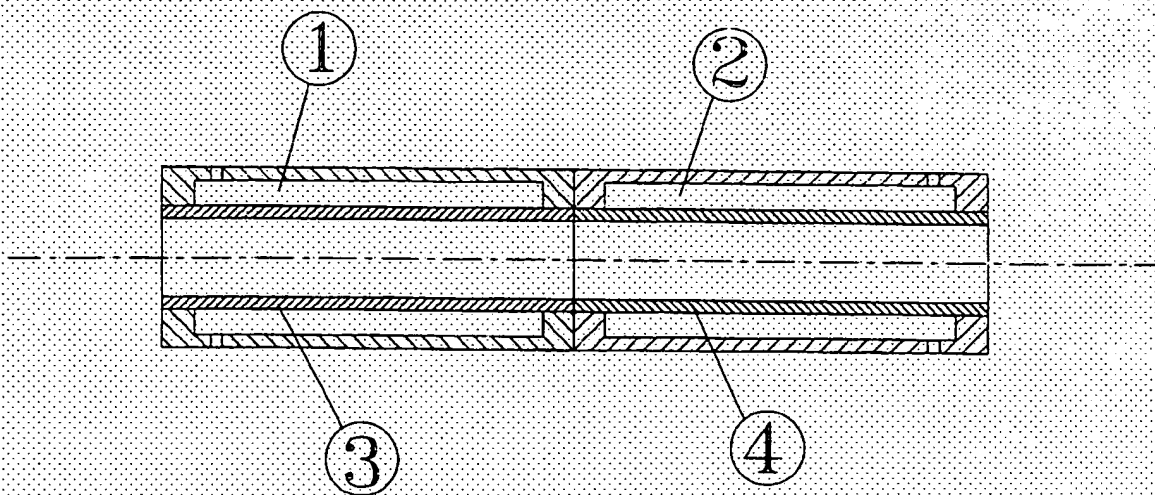


Fig. 8

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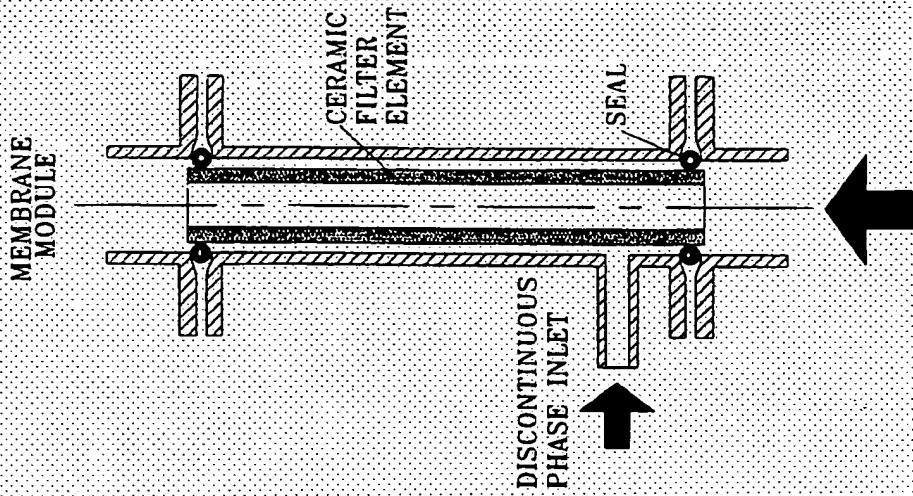


Fig. 11a

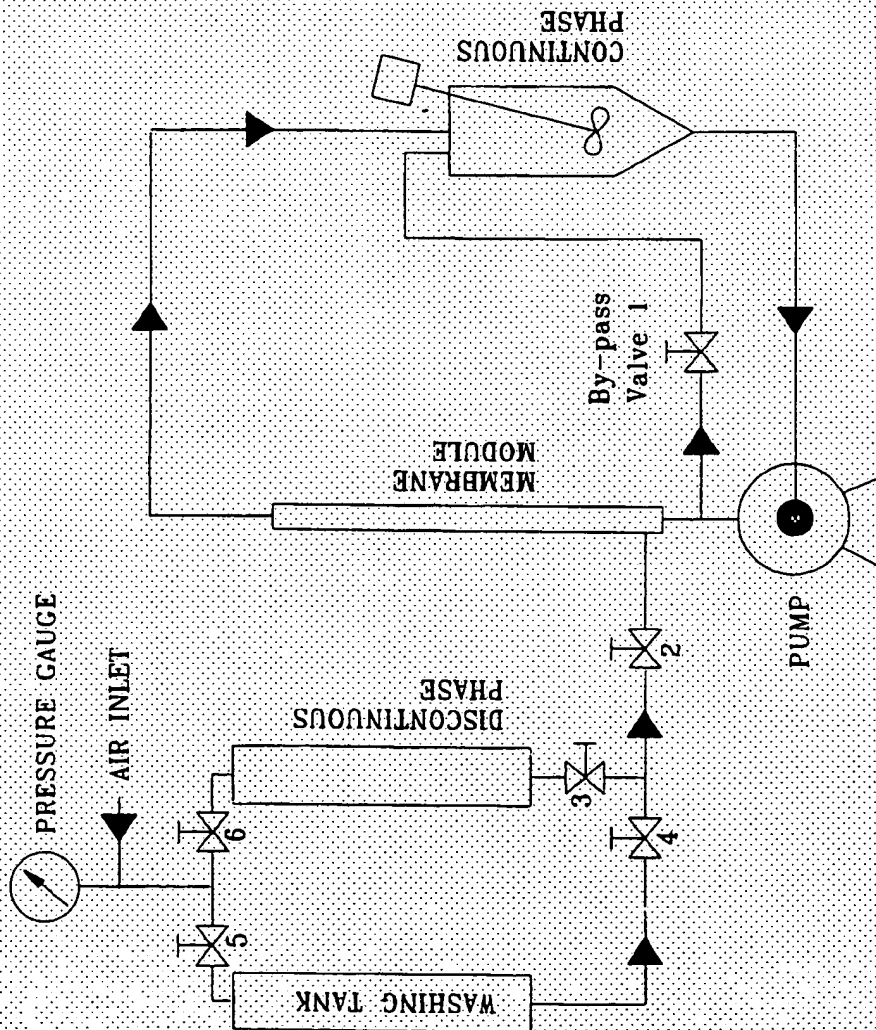


Fig. 11

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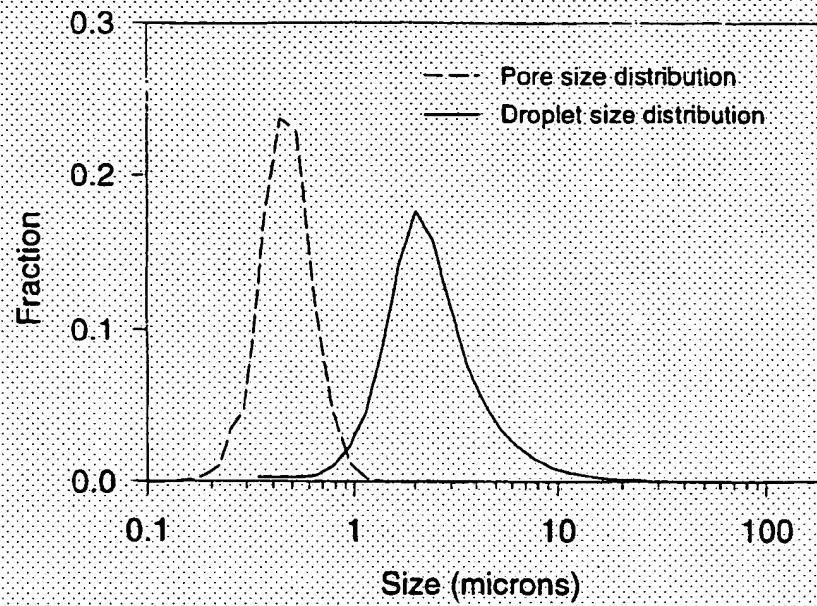


Fig. 12



Fig. 12 (a)



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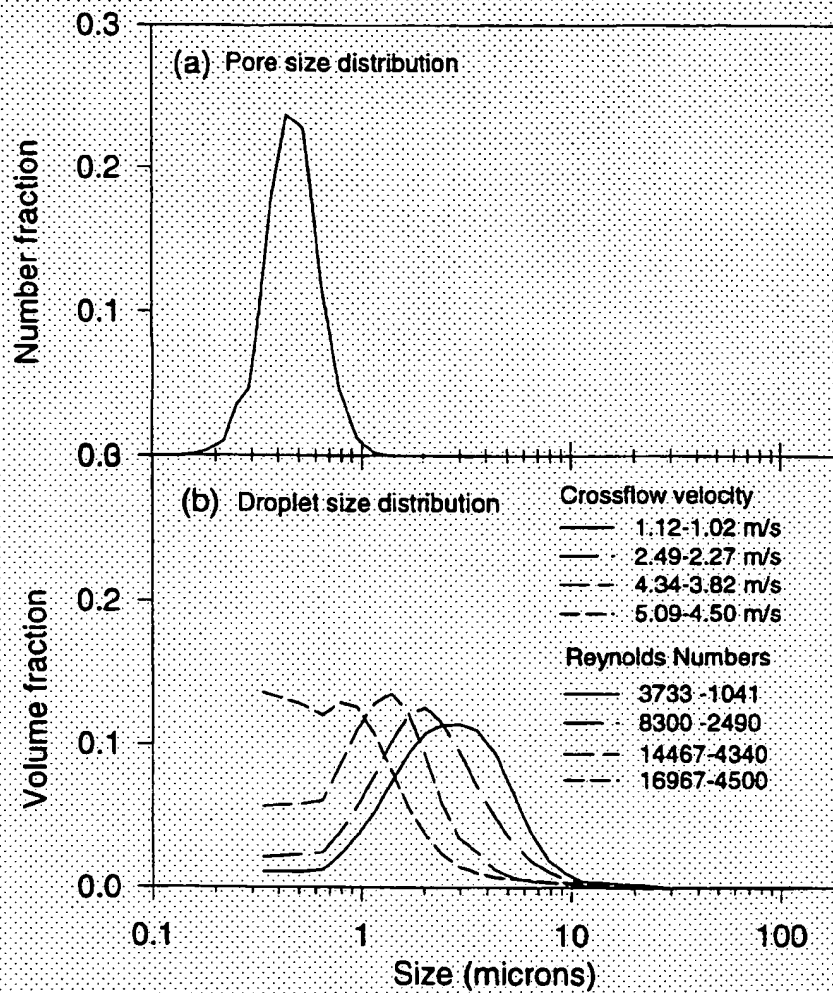


Fig. 13

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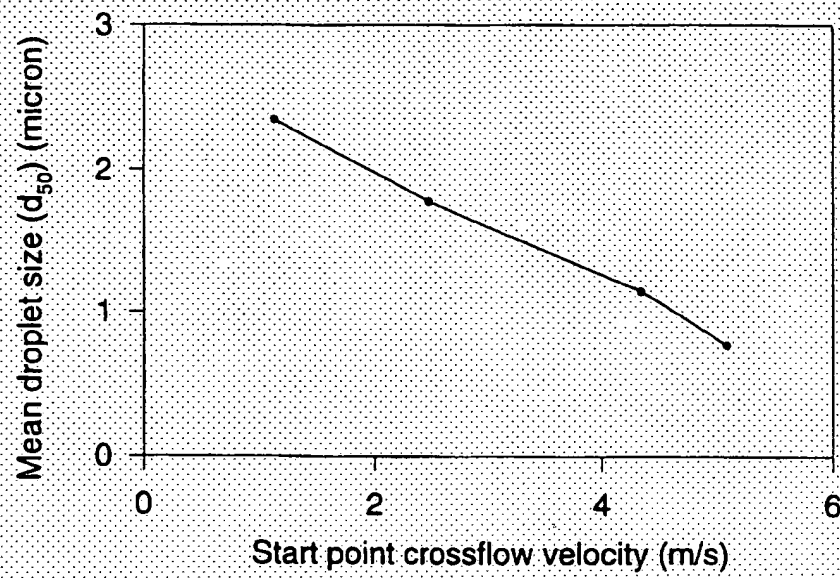


Fig. 14

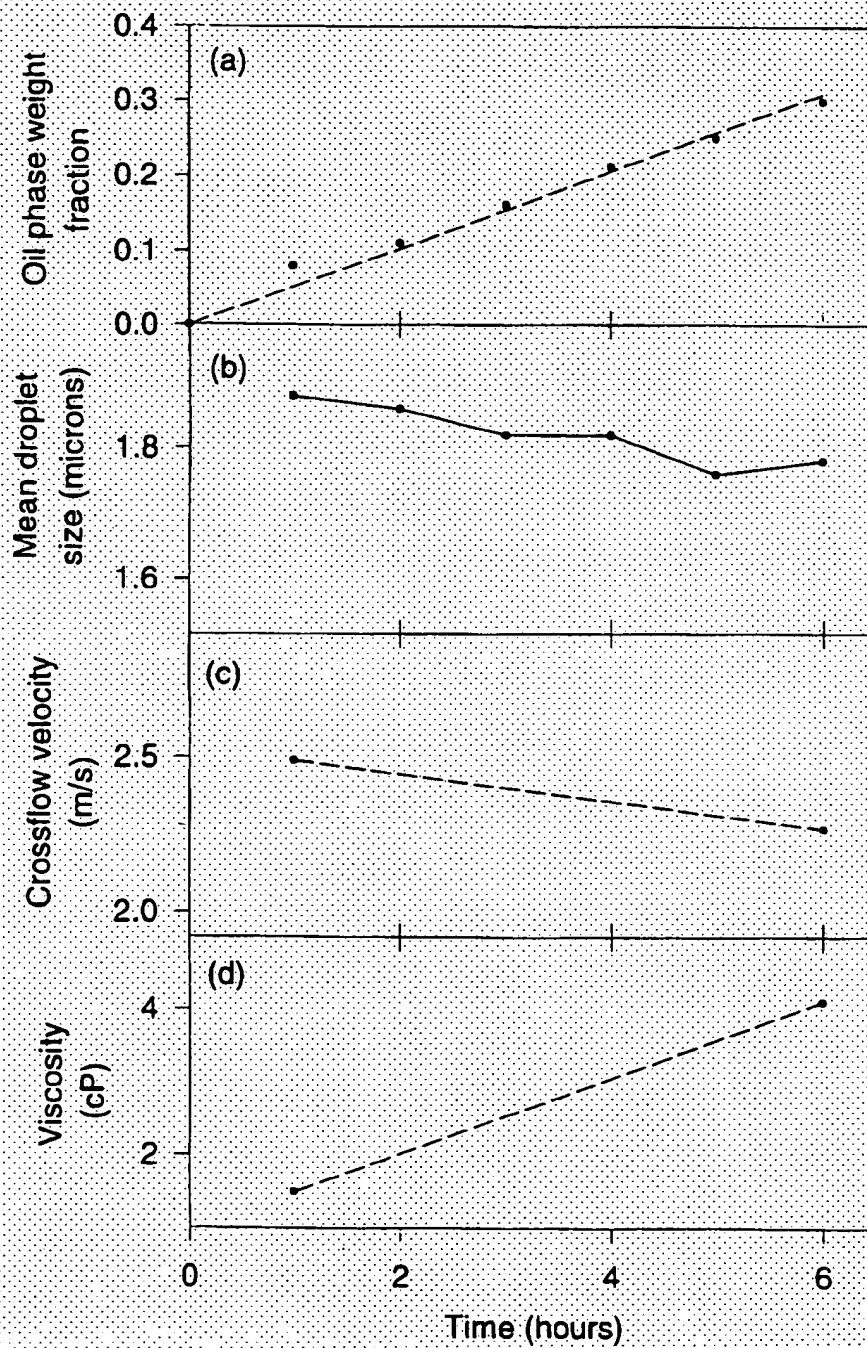


Fig. 15

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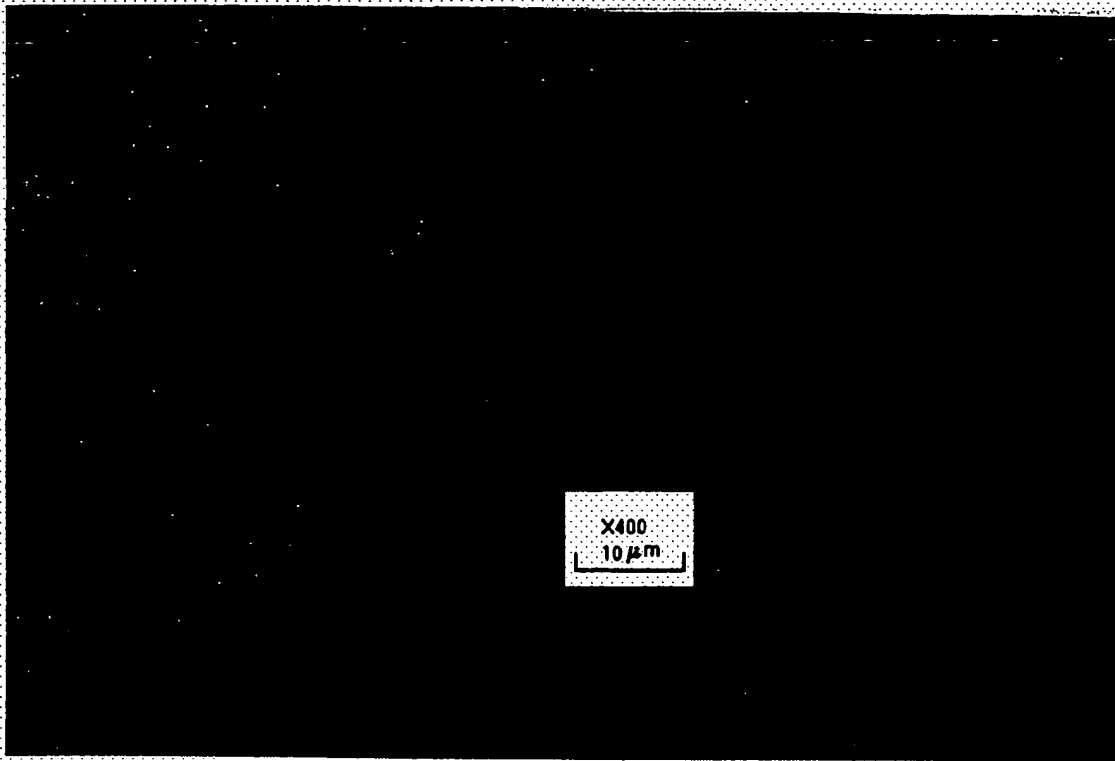


Fig. 16

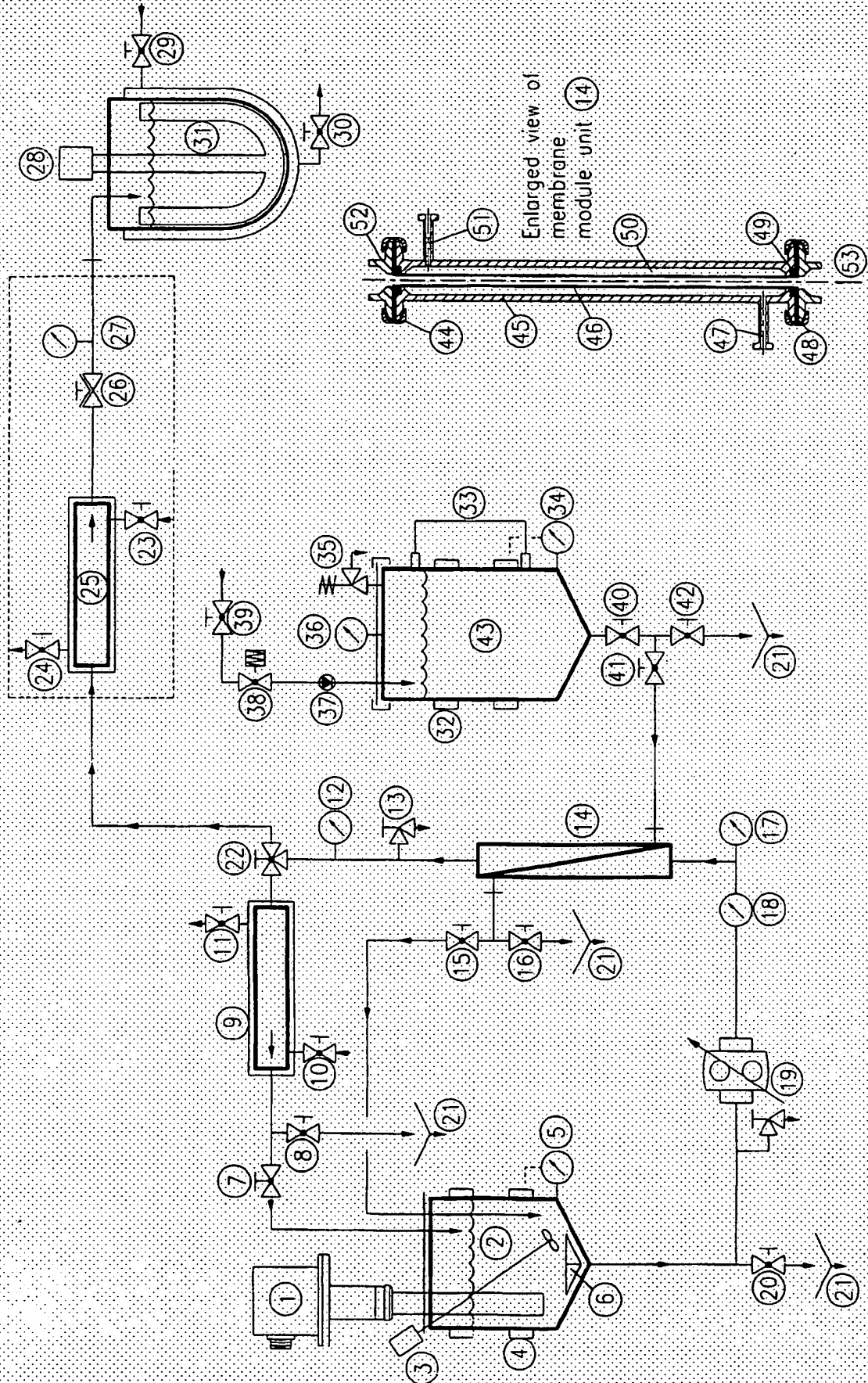










Fig. 21a

Fig. 21



Time (ms)	0	100	240	420	820	2380
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$V=0.40 \text{ m/s}$						

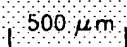
500  $\mu\text{m}$ 

Fig. 22

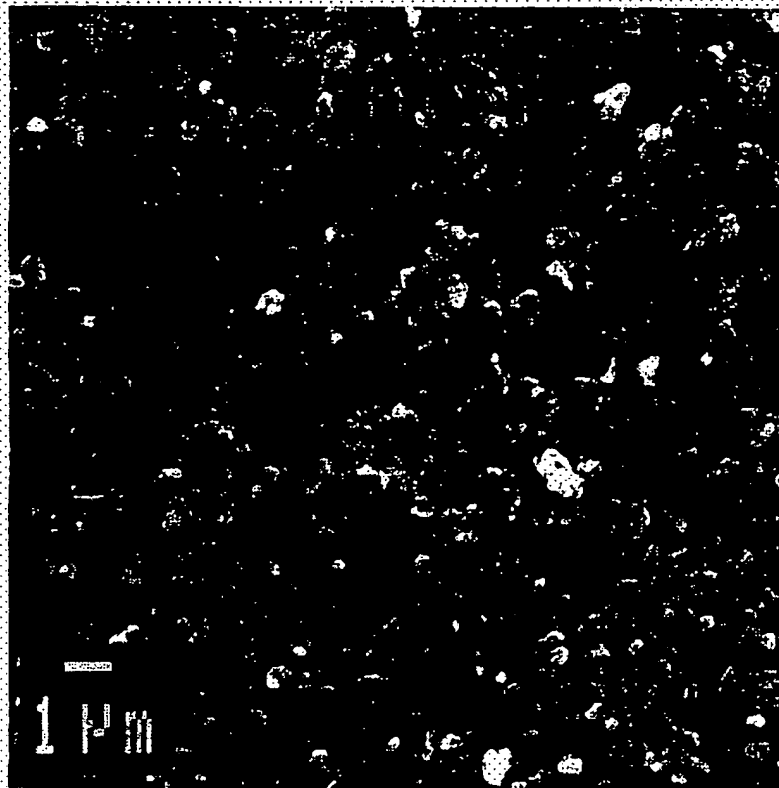


Fig. 23a

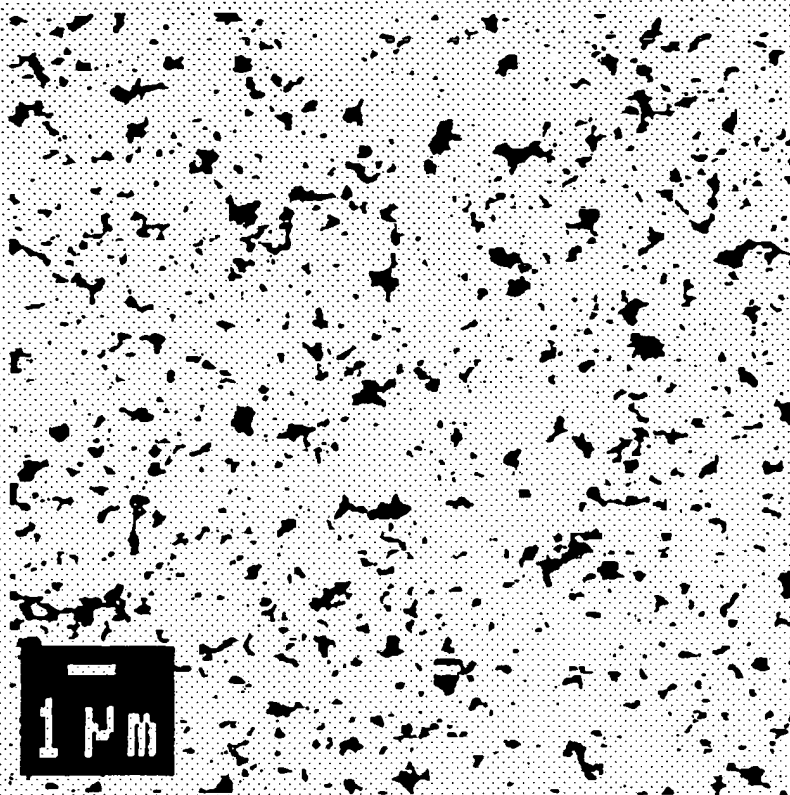


Fig. 23b

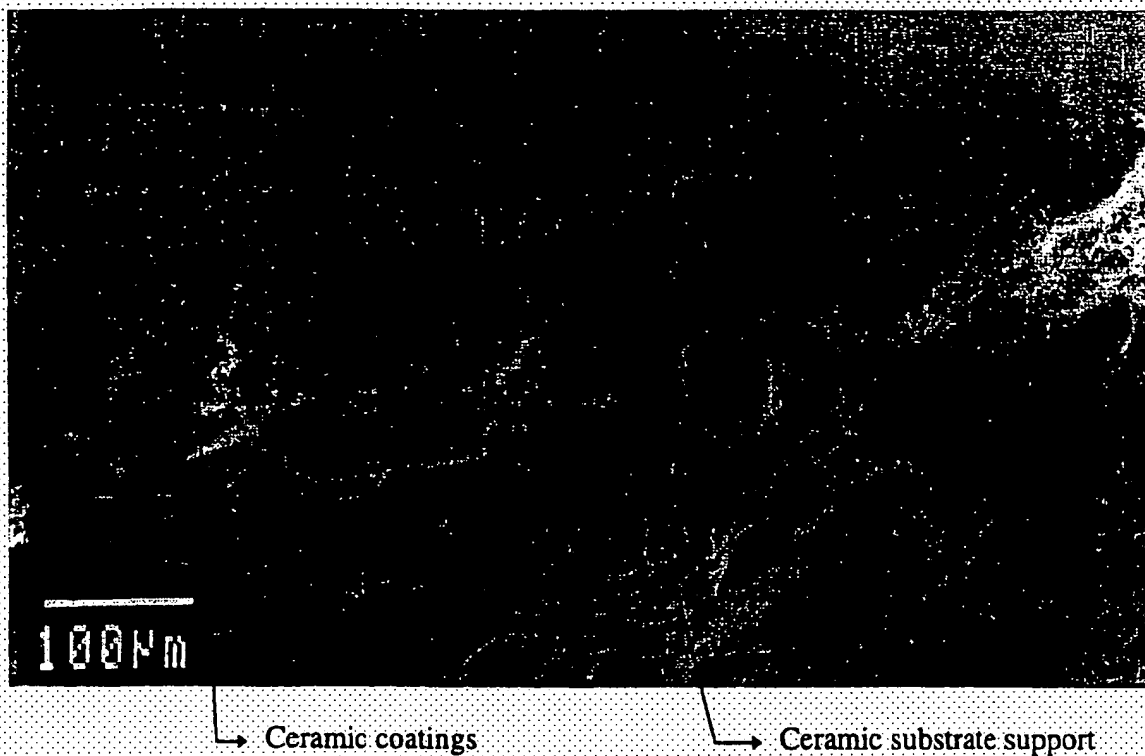


Fig. 23c

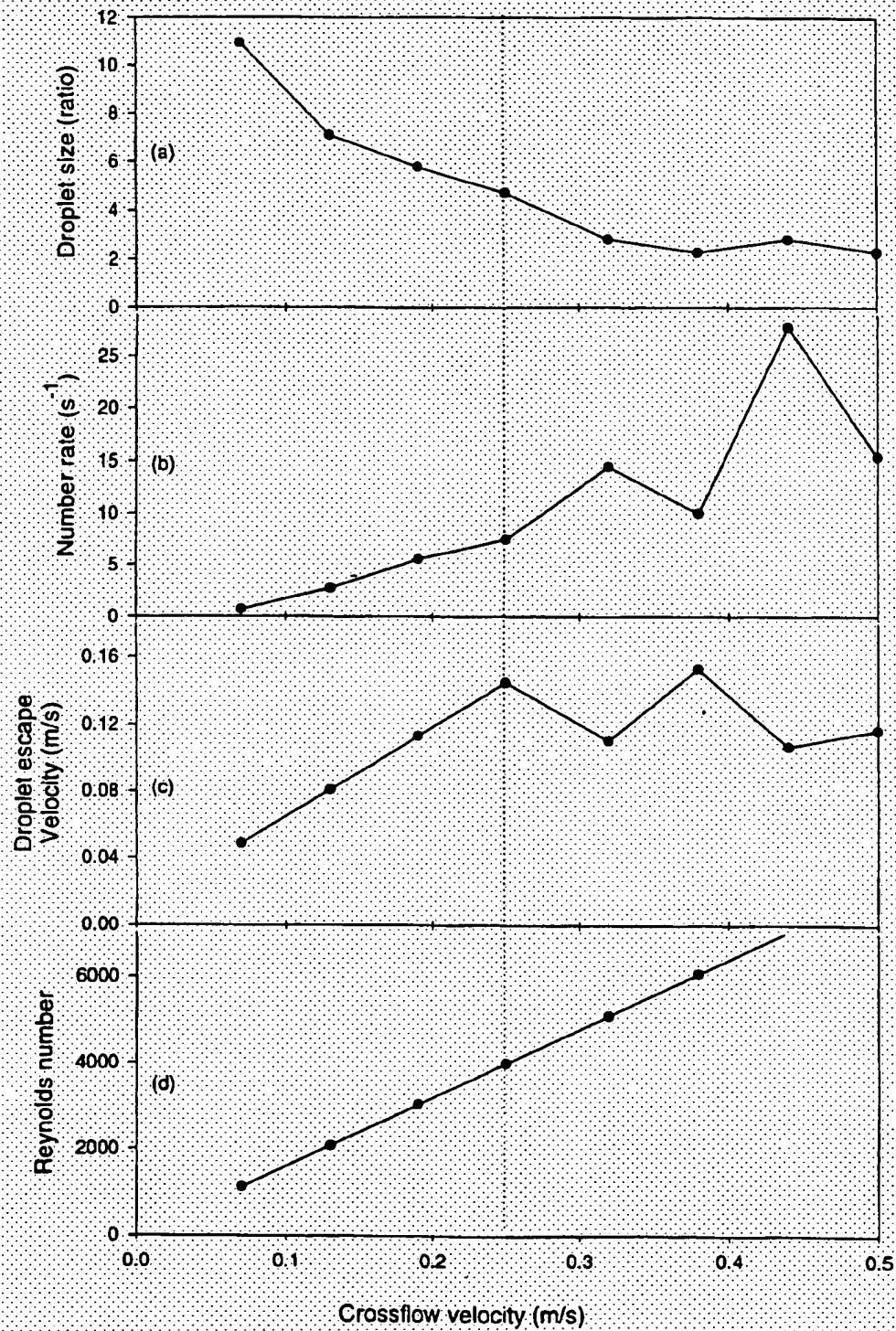


Fig. 24

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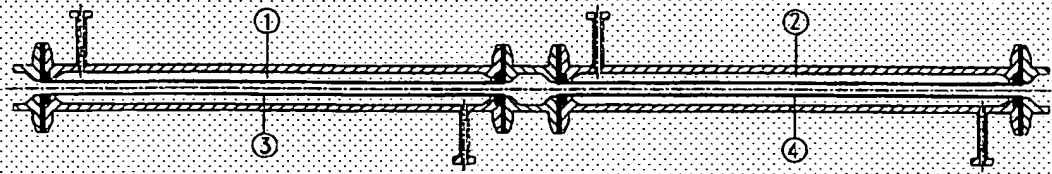


Fig. 26

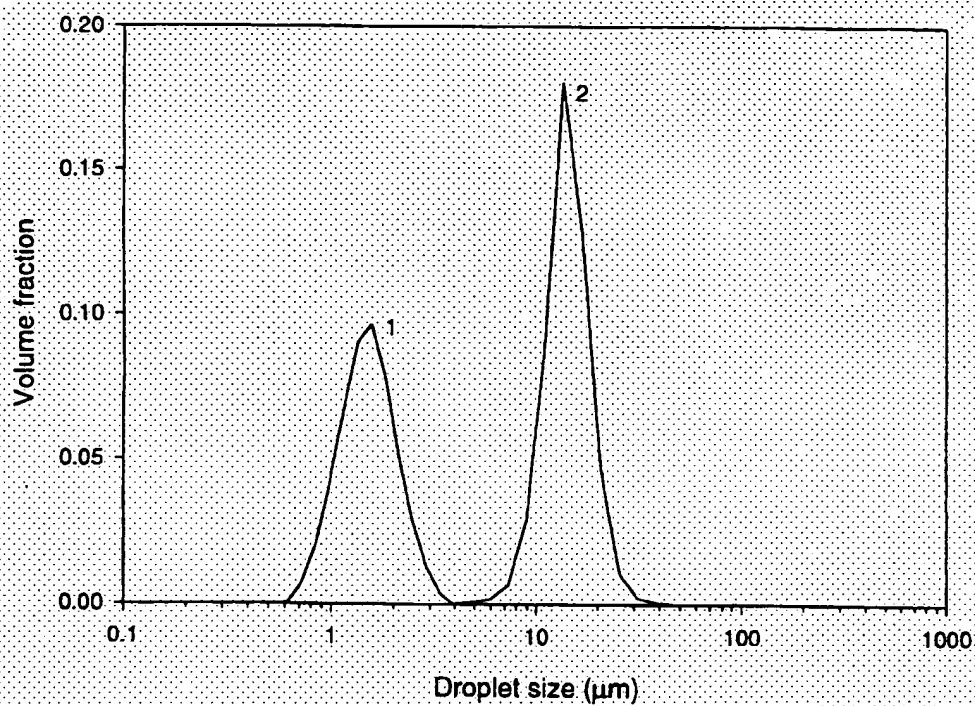


Fig. 27

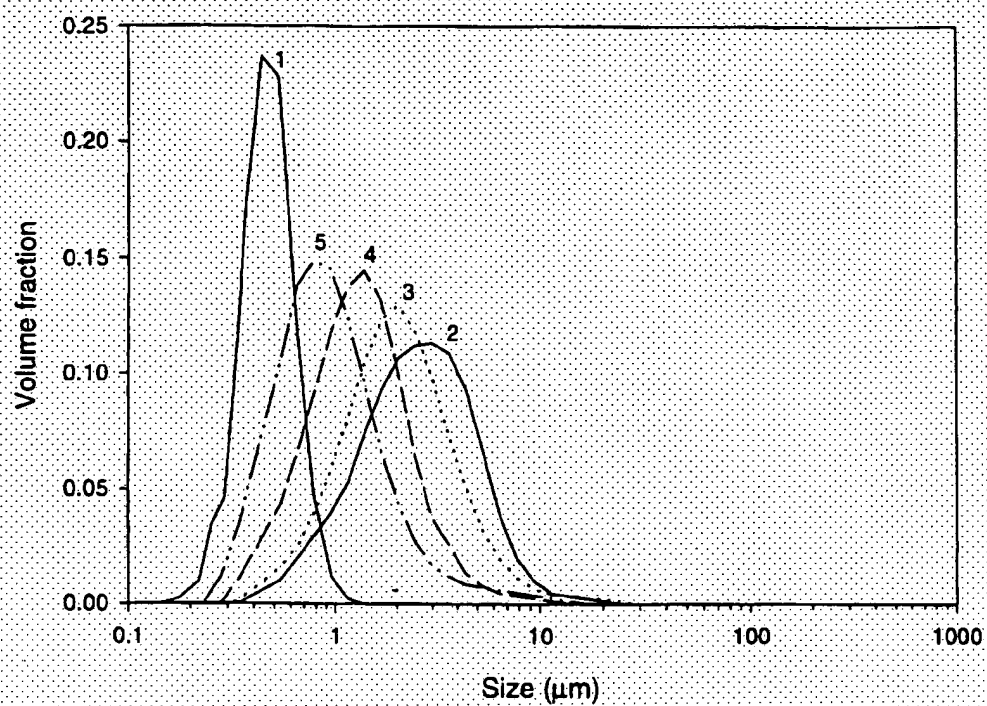


Fig. 28

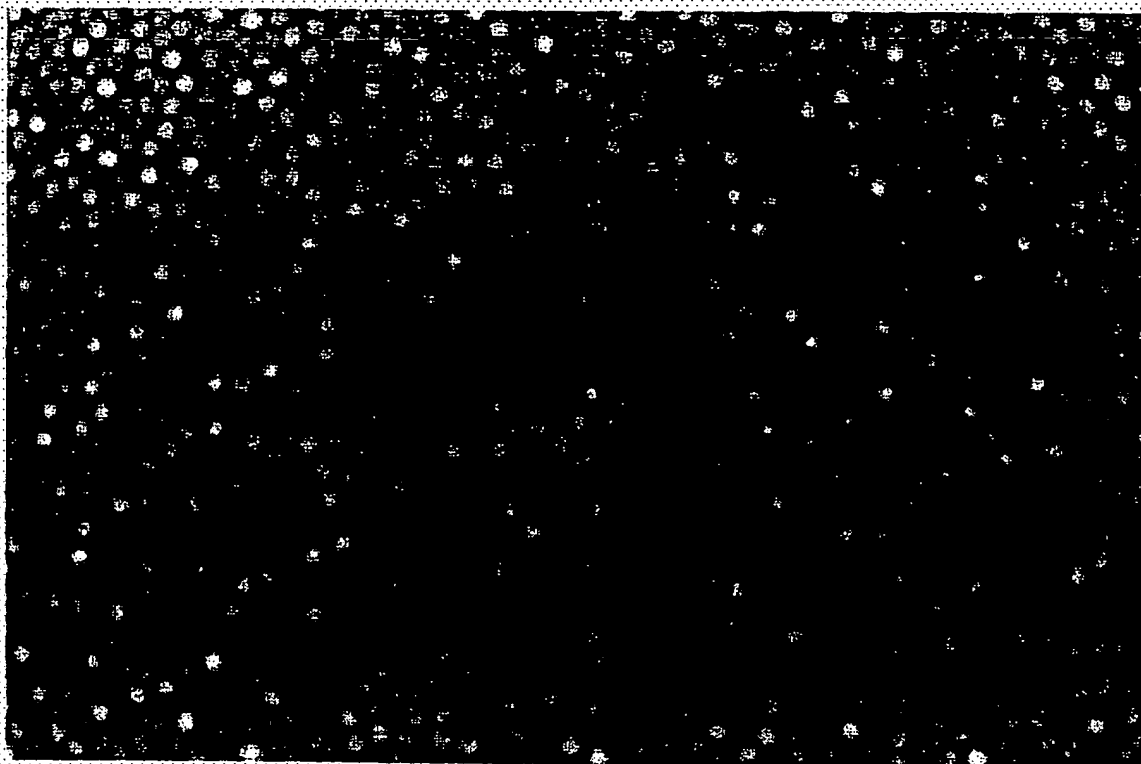


Fig. 29

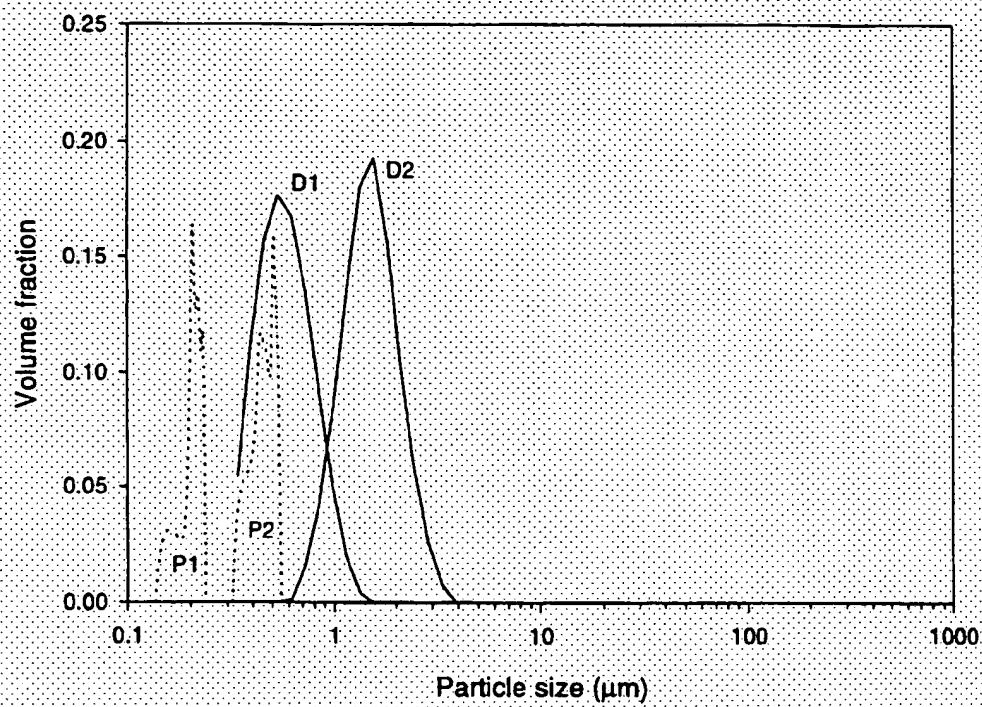


Fig. 30



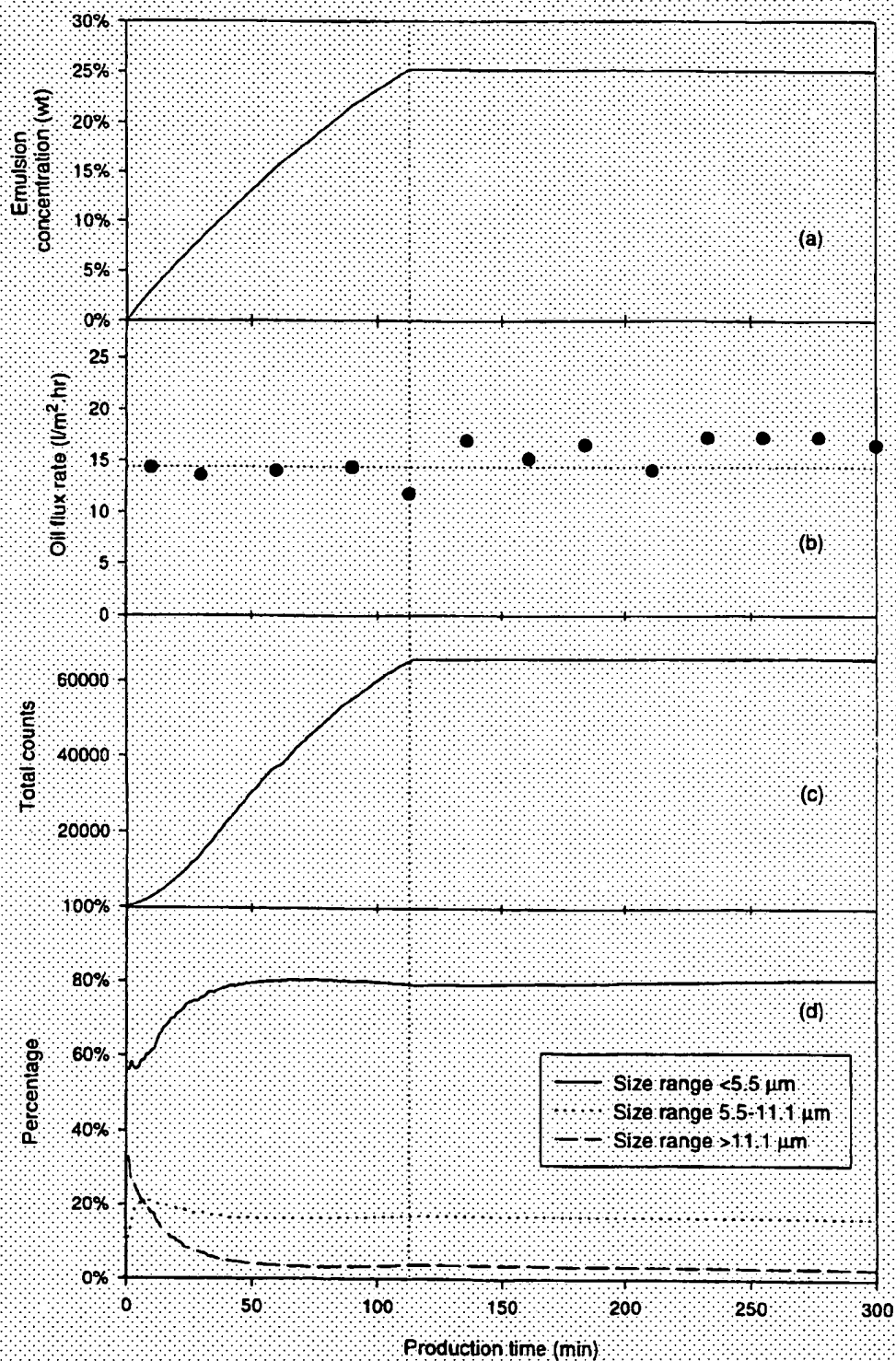


Fig. 31  
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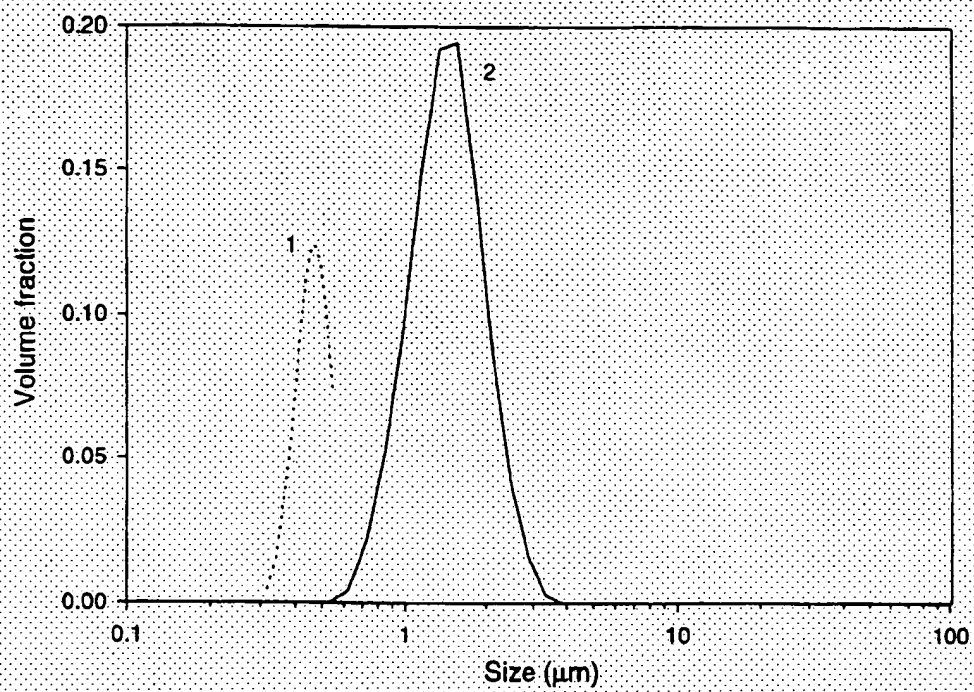


Fig. 32

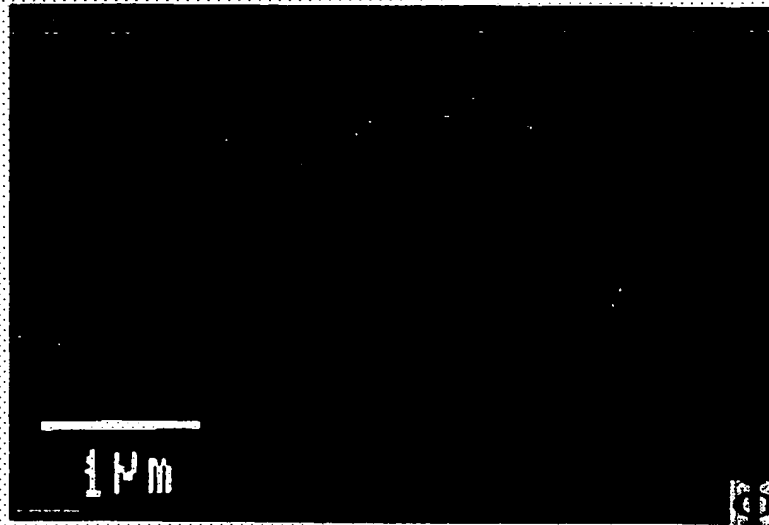


Fig. 33a

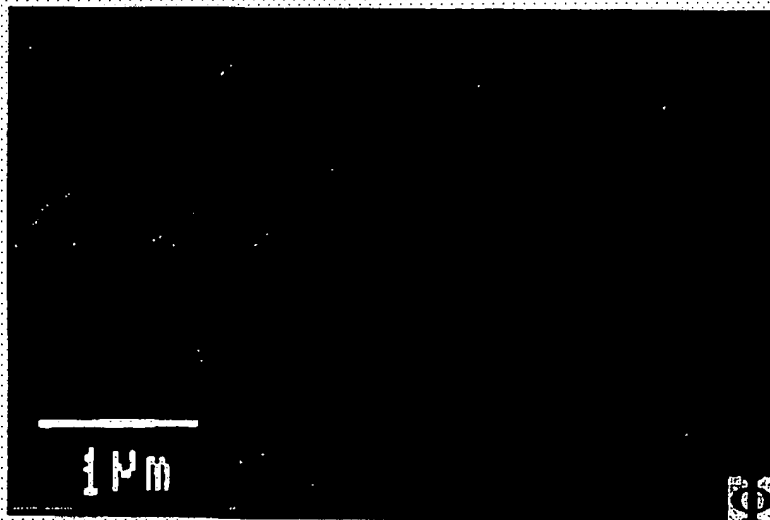


Fig. 33 b

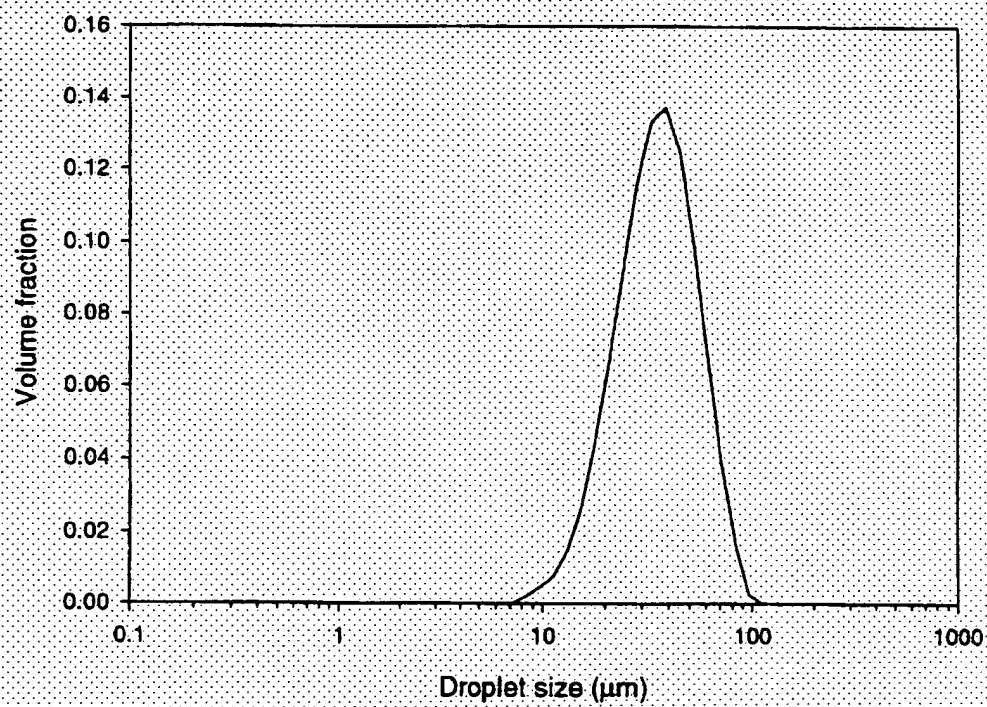


Fig. 34

## INTERNATIONAL SEARCH REPORT

International Application No.

PC 97/00910

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B01F3/08 B01F5/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 564 738 A (MORINAGA MILK INDUSTRY CO LTD) 13 October 1993	1-4
A	see page 3, line 41 - page 4, line 44; figures 1,2	5
X	EP 0 452 140 A (MORINAGA MILK INDUSTRY CO LTD) 16 October 1991 cited in the application see page 3, line 47 - page 8, line 16; claims; figure	1-3
X	EP 0 546 174 A (MIYAZAKI KEN) 16 June 1993 cited in the application	1,3,4
A	see claims; figures 1-5; example 3	8
	-/--	



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Patent family members are listed in annex.

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Date of the actual completion of the international search

17 July 1997

Date of mailing of the international search report

30.07.97

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# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/JP92/00910

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 3 748 277 A (WAGNER J) 24 July 1973 see claim 1 ---	5
A	US 4 147 551 A (FINNICUM LOREN T ET AL) 3 April 1979 see column 2, line 50 - column 3, line 45; figure -----	8

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PC 97/00910

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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